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# Investigation of the Properties of Fully Reacted Unstoichiometric Polydimethylsiloxane Networks and Their Extracted Network Fractions

Sarah Maria Grundahl Frankær · Mette Krog Jensen · Anca Gabriela Bejenariu · Anne Ladegaard Skov

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**Abstract** We investigated the linear dynamic response of a series of fully reacted unstoichiometric polydimethylsiloxane (PDMS) networks and of the two corresponding network fractions namely the sol and the washed network. The sol and the washed network were separated by a simple extraction process. This way it was possible to obtain rheological data from the washed network without interference from the sol fraction, and furthermore from the sol fraction without interference from the elastic washed network. When the stoichiometry increased towards perfectly reacted networks and beyond we observed harder networks both qualitatively and by rheology and the properties of the two fractions became more and more different. At the gel point, the sol fraction and the washed network have more or less identical properties which our data also shows. The storage and loss moduli,  $G'$  and  $G''$ , were analysed with the gel equation as proposed by Winter and Chambon(1986; 1987). We observed that one of the investigated samples which before the swelling experiment did not show any elastic response gave an elastic washed network after swelling, this was verified by analysis with the gel equation. We also calculated the weight fraction of the sol fraction by using the theory by Villar et al. (1996) and compared these with experimentally found values.

**Keywords** Polymer networks · Gel · Soluble structures · Rheology · Linear viscoelastic properties

## 1 Introduction

Polymer networks are widely used as "damping materials" to suppress vibrations and noise and in other materials where a high loss tangent (i.e. large dissipation of energy) at a given frequency range is desirable. Urayama et al. (2004) investigated

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the damping properties of irregular polydimethylsiloxane (PDMS) networks and showed that rather than relying on the glass transition as the energy dissipation one could utilize the temperature and frequency independent dissipation of deformation energy via the viscoelastic relaxation of irregular networks. By washing the networks they removed the sol fraction which is responsible for the energy dissipation and thereby it was possible to get a response from the "pure" washed network without the interference of the sol fraction. This behaviour is difficult to predict but as Urayama et al. (2004) showed the individual contributions can be found experimentally.

Winter and Chambon (1986; 1987) performed several studies on addition curing silicones where they investigated the structural development of the networks by means of rheological characterization by dynamical measurement analysis (DMA). They showed that it was possible to cool down the silicone samples and stop the curing reaction completely. Thereby they investigated perfect networks (i.e. networks where the stoichiometric imbalance,  $r$ , equals 1) as function of the extent of reaction.

In this study a number of fully reacted PDMS samples with stoichiometric imbalances between 0.73 and 1.07 were investigated by rheology before and after removal of the sol fraction. This approach is significantly different from the studies by Winter and Chambon (1986; 1987) since we did not need to control the extent of reaction for the curing process.

We were interested in the dynamics of the initial network as well as the dynamics of the sol fraction and the "pure" washed network. We used a simple extraction procedure to remove the sol fraction; the networks were swelled in solvent and after 48 hours the solvent and the swelled sample were separated and the solvent was allowed to evaporate. This way we could recover the washed network and the sol fraction, respectively (Nandi and Winter, 2005). If any volatiles were present in the system they would also be removed with the solvent. The frequency dependence of the storage and loss moduli,  $G'$  and  $G''$  respectively, for all samples was determined. Thereby we could investigate the dynamics of each the network fractions without interference from the other.

### 1.1 Networks

The networks were made by endlinking PDMS-chains with a trifunctional cross-linker in an addition curing process (Bejenariu et al, 2010). During the process the material changed from being a large number of individual and finite molecules into in theory, one large infinite molecule (Chambon and Winther, 1987). This abrupt change is denoted the gel point and has been investigated to a large extent for networks of different types and with different stoichiometries. The stoichiometric imbalance of the network,  $r$ , is defined as:

$$r = \frac{[\text{hydride}]}{[\text{vinyl}]} = \frac{f [\text{cross-linker}]}{2 [\text{PDMS}]} \quad (1)$$

where  $f$  is the functionality of the cross-linker,  $[\text{cross-linker}]$  and  $[\text{PDMS}]$  are the concentrations of the cross-linker and the PDMS, respectively.  $r$  expresses the relationship between the active functional groups. For  $r < 1$  there is excess PDMS and some chains will not be part of the cross-linking process, for  $r \geq 1$  the

opposite situation is present and all PDMS molecules should be linked to a cross-linker molecule. Another important definition is that of the critical stoichiometric imbalance  $r_c$ :

$$r_c = \frac{1}{f-1} \quad (2)$$

Values of  $r$  below  $r_c$  will not result in the formation of networks.

For an ideal network the system should contain only one great molecule, where all coupling points are connected to the networks. However, practice shows that cross-linking of finite polymers to form a network gives a system with at least two phases; the washed polymer network and the sol fraction (Nandi and Winter, 2005).

We expect that the structure of the molecules in the sol depends highly upon the extent of reaction. In general the formed networks have excess of PDMS-chains to cross-linker, meaning that closely above the gel point the sol fraction will consist of many different types of structures namely unreacted chains, inactive species, chains with only one active site, fully reacted cross-linker molecules and larger more complex structures. Moving towards fully reacted networks the structure of the molecules in the sol will be more uniform. In general the sol will consist of unreacted and inactive chains, chains with one active site and fully reacted cross-linker molecules. The washed network consists of elastically active network chains, i.e. PDMS chains connected in both ends to the network and reacted with a cross-linker. So in the washed network we would expect to see dynamics caused by the elastically active network and the dangling chains and substructures (Hild, 1998). For  $r < 1$  the washed network will have a higher value of  $r$  compared to the initial network while the sol fraction will have a lower value since we primarily are looking into cross-linker deficient networks.

In the close vicinity of the gel point we should be able to part our solution into two fractions and obtain almost identical dynamics of these two fractions. As we proceed beyond the gel point, it should not be (in theory) possible to separate the mixture into two parts. It is therefore clear that in a close range around the gel point we will obtain similar properties of both the sol fraction and the washed network. However, the gel is very soft and may break so a separation may be very difficult.

According to Flory's theory of an ideal cross-linking reaction the PDMS system should become a network for stoichiometric imbalances in the range of  $r = 0.5 - 2$ . Slightly higher values of  $r$  are however anticipated here to compensate for the non-ideal behaviour of the reaction (Flory, 1941a,b, 1953).

## 2 Experimental

### 2.1 Sample Preparation

A series of networks of PDMS were prepared by endlinking of divinyl terminated PDMS (DMS-V31,  $M_n = 28000$  g/mol, Gelest Inc.) with a three-functional cross-linker, phenyltris(dimethylsilyloxy)silane (HMS, Gelest Inc.). A platinum-cyclovinylmethylsiloxane complex (511, Hanse Chemie) was used as catalyst. The chemicals were used as received. The networks were prepared in two rounds with use

**Table 1** Preparation of the applied mixtures A and B.

Mix	PDMS/g	Catalyst/g	Cross-linker/g
A	50	-	0.66
B	50	0.035	-

of two different batches of PDMS. In the first round of experiments networks with  $r = 0.73, 0.75, 0.85, 0.95$  and  $1.07$  were made, and in the second round of experiments networks with  $r = 0.80, 0.84, 0.91$  and  $1.00$  were made.

The networks were made in simple weight based ratios from two ready-made mixtures of PDMS and cross-linker (Mixture A) and PDMS and catalyst (Mixture B) respectively, see Table 1. The A and B mixtures were made beforehand by mixing the components and stirring until complete mixing was obtained. **More details about the mixing procedure can be found in Larsen et al.(2003)**

The networks were made by mixing predetermined amounts of mixture A and B thoroughly and leave the mixture to cure for 12 hours. Mixture A and B were combined in different ratios resulting in networks with different  $r$ -values.

## 2.2 Swelling of Networks

The networks were swelled in heptane (10-15 times excess, i.e. app. 35-50 mL solvent to a sample of 3.5 g, in all experiments we made sure that the PDMS-network were fully covered in solvent) for 48 hours. After the 48 hours the networks were separated from the heptane solution. The heptane was removed by evaporation over 48 hours under atmospheric conditions. The procedure resulted in two samples which were analysed; the washed network and the corresponding sol fraction.

## 2.3 Small Amplitude Oscillatory Shear Measurements

The samples were measured in small amplitude oscillatory shear (SAOS). The measurements were made with a TA 2000 Rheometer from TA Instruments set to a controlled strain mode, the strain was set to 2 % which was ensured to be within the linear viscoelastic regime. The measurements were done with parallel plate geometry of 25 mm in the frequency range from 100 Hz to 0.01 Hz and at temperatures between 0 and 200 °C. After the measurements were done the data was shifted to 25°C using the time-temperature superposition principle (TTS).

## 3 Results and Discussion

The initial PDMS-samples with low  $r$ -values were liquid-like and very soft both before and after swelling. The samples with  $r$ -values above 0.90 were rubbery but slightly greasy to the touch before swelling. The greasy feel disappeared after the washing procedure.

From the experimentally determined weight fraction of sol,  $W_{\text{sol}}$  (Table 2 and Figure 1), it is obvious that an ideal network with no sol fraction is not obtained.

**Table 2**  $r$ -values, weight percentages (weight-%) and  $W_{\text{sol experimental}}$  for the networks. The measurements are averages of data from 2-6 samples, except for  $r=0.71$  where only one sample was available

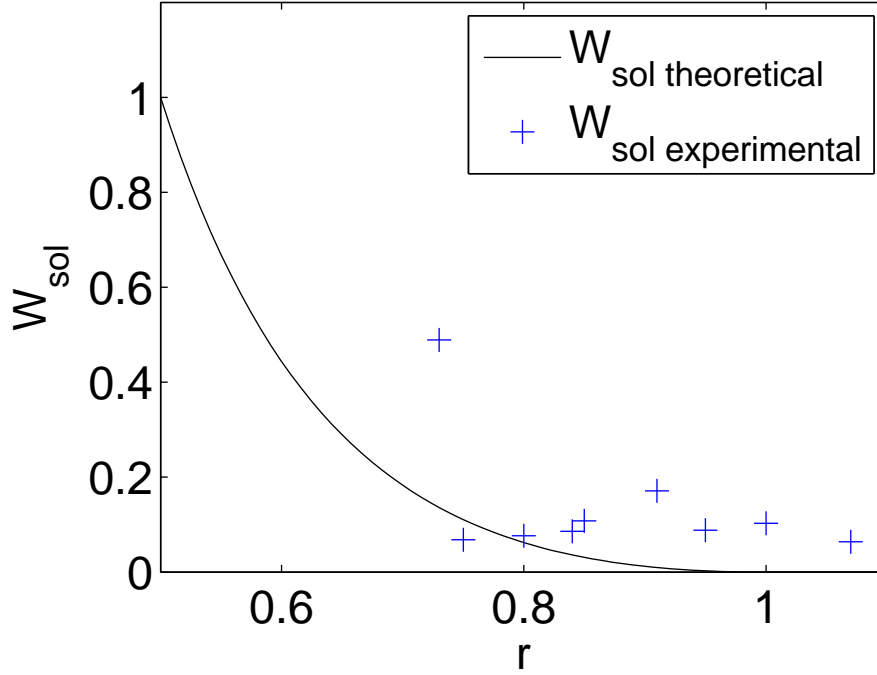
$r$	Weight-% PDMS	Weight-% cross-linker	Weight-% catalyst	$W_{\text{sol experimental}}$
$0.73 \pm 0.02$	$99.3 \pm 0.017$	$0.667 \pm 0.018$	$0.034 \pm 0.001$	$0.489 \pm 0.141$
0.75	99.3	0.684	0.033	0.068
$0.80 \pm 0.02$	$99.2 \pm 0.016$	$0.736 \pm 0.016$	$0.031 \pm 0.001$	$0.077 \pm 0.045$
$0.84 \pm 0.02$	$99.2 \pm 0.019$	$0.771 \pm 0.021$	$0.046 \pm 0.002$	$0.086 \pm 0.034$
$0.85 \pm 0.00$	$99.2 \pm 0.002$	$0.782 \pm 0.002$	$0.028 \pm 0.000$	$0.108 \pm 0.043$
$0.91 \pm 0.01$	$99.1 \pm 0.012$	$0.834 \pm 0.013$	$0.026 \pm 0.000$	$0.171 \pm 0.034$
$0.95 \pm 0.00$	$99.1 \pm 0.002$	$0.869 \pm 0.002$	$0.023 \pm 0.000$	$0.088 \pm 0.047$
$1.00 \pm 0.02$	$99.1 \pm 0.017$	$0.910 \pm 0.017$	$0.021 \pm 0.001$	$0.103 \pm 0.002$
$1.07 \pm 0.00$	$99.0 \pm 0.003$	$0.979 \pm 0.003$	$0.017 \pm 0.000$	$0.064 \pm 0.019$

It rather seems that for values of  $r$  around and above 1 we obtain a value between 5 – 10% sol fraction, which gives a clear indication of inactive species within the polymer and imperfections in the formed network. Furthermore for values of  $r$  approaching 0.7 it seems that there is a large variation in  $W_{\text{sol}}$  which corresponds well with that  $r$  is approaching  $r_c$  and hence the mixing is critical for reproducibility. For slow mixing procedures we observed heterogeneity in the mixes so a fast and immediate mixing procedure had to be applied. From Equation 2 it is obvious that when  $f = 3$  then  $r_c = \frac{1}{2}$ . This value indicates the gel point with respect to the stoichiometry. The high value of the stoichiometric imbalance at the experimentally determined gel point may be due to steric hindrance of the cross-linker. In order to clarify if steric hindrance was a kinetic problem we investigated the curing profiles obtained in the rheometer at a constant frequency of 1 Hz where we followed the structural development of the networks for several hours. Post-curing processes could not be detected within 5 hours after a constant level in  $G'$  and  $G''$  had been reached, and we therefore conclude that our procedure ensured complete reaction. In Figure 1 the theoretical weight fraction of the sol fraction,  $W_{\text{sol theoretical}}$ , is plotted along with the experimentally found  $W_{\text{sol experimental}}$ . The experimental data shows the same tendency as the theory, however,  $W_{\text{sol}}$ , is more constant and higher around  $r = 1$  than expected.

### 3.1 SAOS Data

Figures 2 to 4 shows the dynamics for the initial networks, the sol fractions and washed network, respectively. If we look at the data for the initial samples (Figure 2) is observed that samples with  $r$  above 0.84 act as viscoelastic solids indicated by the plateau seen for  $G'$  at low frequencies. The networks with  $r = 0.73$  and  $r = 0.75$  behaves as viscous materials, while the sample with  $r = 0.80$  must be close to the gel point since  $G' \approx G''$  in the entire frequency range.

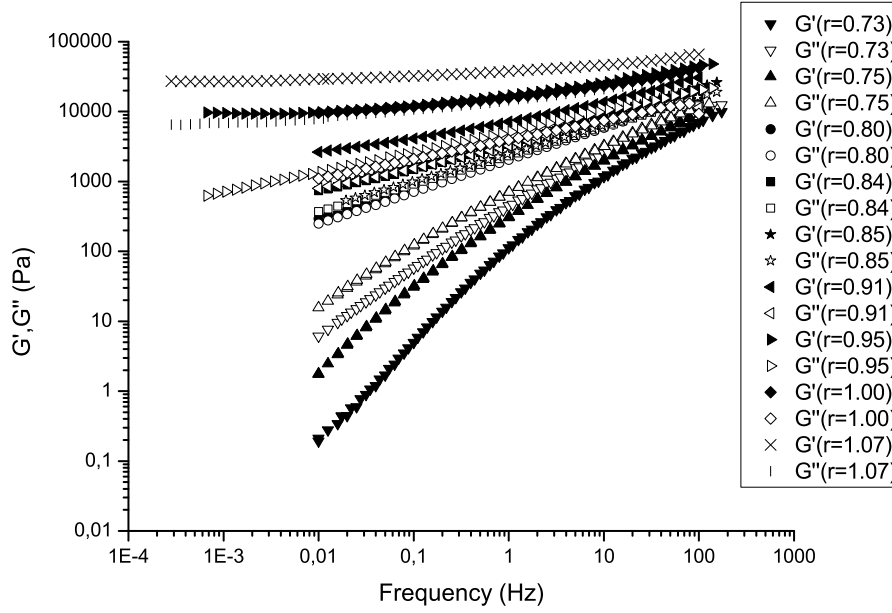
**For the sol fraction (Figure 3) for  $r = 0.73$  the data shows indications of the presence of a physical network of long entangled PDMS-chains. For  $r = 0.75$  the sol fraction is viscous.** The sol fraction from the sample with  $r = 0.80$  again show indications of being close to the gel point. For the samples with higher stoichiometric imbalances the results show no general tendency. In



**Fig. 1** Comparison of experimentally found and theoretical values of  $W_{\text{sol}}$

some of the samples (mainly  $r = 0.84$ ,  $r = 0.85$ ,  $r = 0.95$  and  $1.00$ ) a tendency towards elastic properties is indicated by a plateau at low frequencies. However it is observed that the value for the  $G'$ -plateau does not consistently increase with increasing stoichiometry as is observed for the initial networks. We expect that this is related to the structure of the molecules in the sol. We expect that the largest structures in the sol are found for  $r$ -values above the gel point ( $0.5$ ) but not too close to  $1$ . Close to  $r = 1$  we expect the sol to consist mainly of inactive chains and chains with only one active site due to imperfections in the PDMS-polymer.

All the washed networks (Figure 4) with  $r \geq 0.85$  show viscoelastic properties and the value for the  $G'$ -plateau is increasing steadily with increasing  $r$  as expected. The data for the washed network with  $r = 0.73$  indicate that the sample is close to the gel point by having  $G' \approx G''$  in the entire frequency range. Furthermore it is interesting that the washed network with  $r = 0.80$  has  $G' > G''$  in the entire frequency range indicating that the sample is more elastic than viscous, while both the initial network and the sol fraction showed gel point characteristics. For the sample with  $r = 0.75$  we observed that at low frequencies  $G'$  is larger than  $G''$  again indicating elastic response in the sample. For the initial sample with  $r = 0.75$  no elastic response could be detected. In other words it is possible to extract an elastic washed network from a sample which initially show no elastic response. The sol fraction of this sample was able to smear the elastic response out so it was undetectable.



**Fig. 2** The dynamics of the initial networks. The stoichiometric imbalance is given in the figure. The higher the stoichiometric imbalance the more elastic the network. The data was shifted to 25°C by TTS and the strain was set to 2 %

### 3.2 Fitting the Experimental Data to the Gel Equation

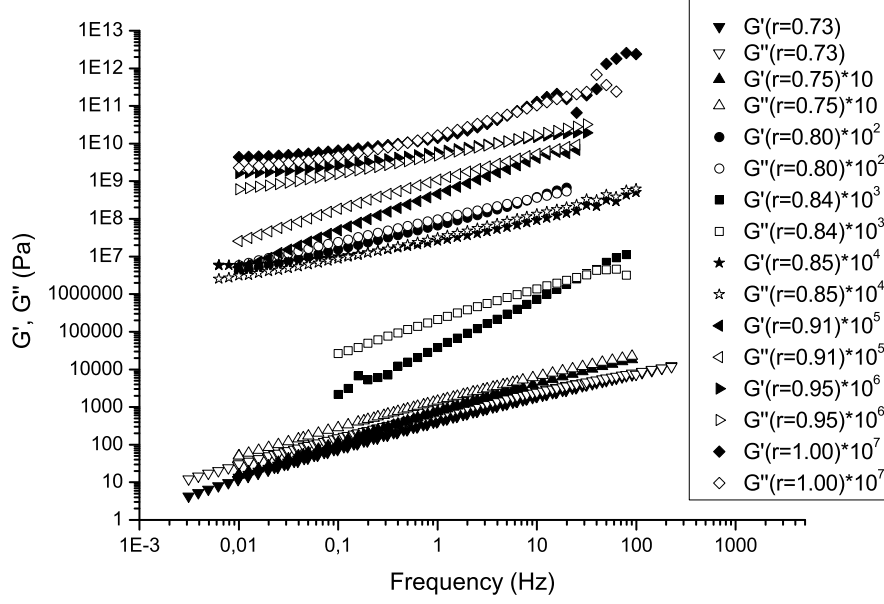
The viscoelastic properties were measured in SAOS-experiments, and the measured  $G'$  and  $G''$  were analysed. In the cases where the PDMS-samples have formed networks beyond the gel point they will behave as viscoelastic solids. This means that a plateau is reached for  $G'$  at the low frequency regime, and it will often be orders of magnitudes higher than the loss modulus,  $G''$ . At higher frequencies  $G'$  and  $G''$  will be of the same order of magnitude, however the plateau regime will increase as the cross-link density increases, hence as  $r$  increases. For gels  $G''$  is following a power law behaviour over the whole frequency range and is thus proportional to  $\omega$ . (Bird et al, 1987; Hild, 1998; Morrison, 2001; Jensen et al, 2009) One way to analyse  $G'$  and  $G''$  is to use the gel equation proposed by Winter and Chambon(1986; 1987):

$$G(t) = St^{-n} \quad (3)$$

From the relaxation modulus it is possible to derive corresponding expressions for  $G'$  and  $G''$  and the relation between  $G'$  and  $G''$  is very simple and can be derived from Equation 3:

$$G'(\omega) = \omega \int_0^\infty G(s) \sin(\omega s) ds = \frac{S\pi\omega^n}{2\Gamma(n) \cos \frac{n\pi}{2}} \quad (4)$$





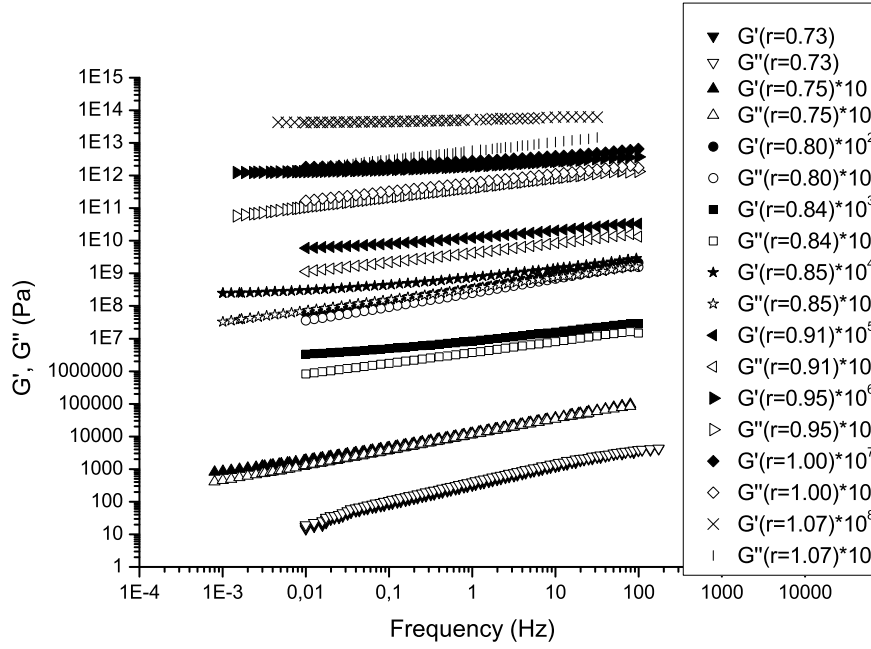
**Fig. 3** The dynamics of the sol fractions. The stoichiometric imbalance of the according initial network is given in the figure. The data was shifted to 25°C by TTS and the strain was set to 2 %

$$G''(\omega) = \omega \int_0^\infty G(s) \cos(\omega s) ds = \frac{S\pi\omega^n}{2\Gamma(n) \sin \frac{n\pi}{2}} \quad (5)$$

$$G' = \frac{G''}{\tan(\frac{n\pi}{2})} \quad (6)$$

Equation 3 is a simple model for the relaxation modulus of a critical gel as a function of time. By critical gel is meant a sample at the gel point where the viscosity is infinite while the equilibrium modulus is zero.  $S$ , in Equation 3, is a measure for the gel stiffness with respect to the number of entanglements of the precursor chains (PDMS-chains), while  $n$  is a relaxation exponent, and it is thus the slope of  $G''$  in a double logarithmic plot. Winter and Chambon (1986; 1987) made a thorough investigation of the size of  $n$  at the gel point, and they found that for a stoichiometric balanced gel ( $r = 1$ )  $n$  was equal to  $1/2$ , and that  $G'$  and  $G''$  would be congruent over the entire frequency range,  $0 < \omega < \infty$ . For stoichiometric imbalanced ( $r \neq 1$ ) gels  $n$  would increase and lie in the range  $1/2 < n < 1$ . Hild (1998) found a similar result for  $r < 1$ , while for  $r > 1$ ,  $n$  was found to be equal to  $1/2$  at the gel point.

A more general indication of the size of  $n$ , can be found in Equation 6, which predicts that if  $n > 1/2$  then  $G'' > G'$ , while  $G'' < G'$  if  $n < 1/2$ . It is important to notice that this analysis has been performed on gels at the gel point. In this study the network are beyond the gel point. When analysing data beyond the gel



**Fig. 4** The dynamics of the washed networks. The stoichiometric imbalance of the according initial network is given in the figure. The tendency towards more elastic networks with higher stoichiometric imbalances is also seen here. The data was shifted to 25°C by TTS and the strain was set to 2 %

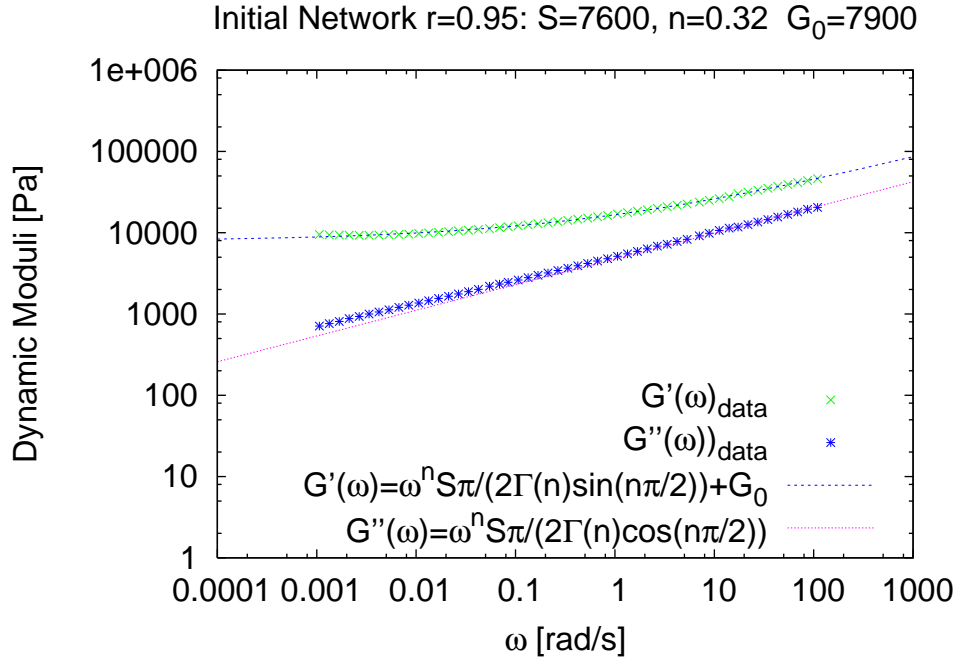
point, it is necessary to modify the gel equation, such that it accounts for the plateau obtained for  $G'$ . This was done by Jensen et. al. (2009) They analysed stoichiometric imbalanced polypropylene oxide networks,  $r < 1$ , cured to complete reaction, by adding an additional term to Equation 3:

$$G(t) = St^{-n} + G_0H(t) \quad (7)$$

where  $H(t)$  is the Heaviside step function, while  $G_0$  is the equilibrium modulus or plateau modulus obtained for  $G'$  at low frequencies. The study by Jensen et. al. (2009) showed that even for gel beyond the gel point  $n$  can change significantly.  $n$  would be high,  $> 1/2$ , for very soft gels, while for  $r \rightarrow 1$  harder gels are obtained and  $n$  could drop to about 0.35. Hence  $n$  is a measure for the softness of the gel (Jensen et al, 2009). A similar analysis of  $n$  will be made in this study with imbalanced PDMS networks, that are also cured to complete reaction.

The modified gel equation given in Equation 7 was used to fit the linear viscoelastic data of the samples at or beyond the gel point. Figure 5 shows the viscoelastic data measured for the initial network with  $r = 0.95$  together with the curves corresponding to Equations 4 and 5. The parameters  $S$  and  $n$  were determined with a least square routine, while  $G_0$  was determined by the plateau given by the experimental data.

The parameters,  $G_0$ ,  $S$  and  $n$  for all the gels are listed in Tables 3 to 5. It is seen that the parameters cannot be determined for the initial networks with  $r = 0.73$ ,



**Fig. 5** The dynamic moduli of the initial network with  $r = 0.95$ . The curves are fits of  $G'$  and  $G''$  with Equations 4 and 5

0.75 and 1.07 and the sol fractions with  $r = 0.73$ , 0.75, 0.80, 0.85 and 1.07. **The reason for this is that many of the mentioned samples are simply not gels and fitting the gel equation to data on samples which are not gels gives problems. We present the fits here because they underline the large differences in the networks fractions.** This is however not the case for the initial network with  $r = 1.07$ , this will be discussed in details later. Interestingly it is possible to determine the parameters for the washed network at  $r = 0.73$  and 0.75. The result shows that the samples with  $r = 0.75$  is in fact beyond the gel point, since  $G'$  levels off to a plateau at low frequencies. This shows that it is possible to extract a network beyond the gel point from a sample that appears not to any elastic characteristics, which was also mentioned earlier, but this is due to change of time scales for relaxation. The initial sample with  $r = 0.80$  showed gel point characteristics in the SAOS-data and the fit to the Equation 4 and 5 underline this since  $n$  is 0.49.

The parameters for the initial network with  $r = 1.07$  could as mentioned earlier not be determined. The reason for this is not clear, however it was not possible to fit both equation 4 and 5 to  $G'$  and  $G''$  at the same time. This indicates that there is not consistency between the data as there should be according to the Kramers-Kronig relation (Bird et al, 1987). The data measured for this sample, along with that for the sample with  $r = 0.73$  where the gel parameters could not be found for any of the parts, will therefore not be used in the discussion given below. Moreover linear viscoelastic data was not obtained for the sol fraction at

**Table 3** Gel parameters,  $G_0$ ,  $S$  and  $n$ , obtained by fitting Equations 4 and 5 to the linear viscoelastic data for the initial networks

$r$	Initial Network		$n$
	$G_0$ [Pa]	$S$ [Pa·s <sup>-1</sup> ]	
0.73	-	-	-
0.75	-	-	-
0.80	140	1700	0.49
0.84	310	2700	0.41
0.85	200	2800	0.39
0.91	2100	4000	0.38
0.95	7900	7600	0.32
1.00	8400	6000	0.31
1.07	-	-	-

**Table 4** Gel parameters,  $G_0$ ,  $S$  and  $n$ , obtained by fitting Equations 4 and 5 to the linear viscoelastic data for the sol fractions. Values in parenthesis are from a fit with high deviation

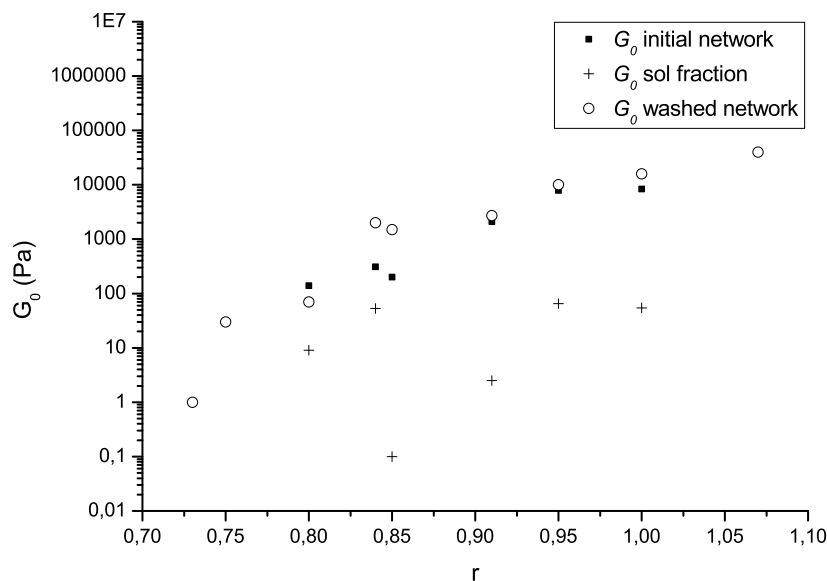
$r$	Sol Fractions		$n$
	$G_0$ [Pa]	$S$ [Pa·s <sup>-1</sup> ]	
0.73	-	-	-
0.75	-	-	-
0.80	(9)	(500)	(0.6)
0.84	53	150	0.64
0.85	(0.1)	(15)	(0.94)
0.91	2.5	200	0.9
0.95	65	440	0.42
1.00	54	40	0.82
1.07	-	-	-

**Table 5** Gel parameters,  $G_0$ ,  $S$  and  $n$ , obtained by fitting Equations 4 and 5 to the linear viscoelastic data for the washed networks

$r$	Washed Network		$n$
	$G_0$ [Pa]	$S$ [Pa·s <sup>-1</sup> ]	
0.73	1	500	0.55
0.75	30	1020	0.46
0.80	70	2800	0.41
0.84	2000	5000	0.35
0.85	1500	6000	0.3
0.91	2700	8600	0.26
0.95	10000	10000	0.26
1.00	16000	10000	0.31
1.07	40000	10500	0.27

$r = 1.07$  because the **amount of sol fraction was too small for rheological characterization.**

All the data in Tables 3 to 5 is plotted vs.  $r$  in Figures 6, 7 and 8. It is seen that both  $G_0$  and  $S$  increases with  $r$ , while  $n$  decreases. This is expected since  $G_0$  is a measure for the elasticity of the network, and therefore as  $r$  increases the more network strands are connected to the elastic active network.  $S$  is a measure for the stiffness with respect to number of trapped entanglements which also will increase as  $r$  increases. Finally the more dynamic the network the higher  $n$ . Similar



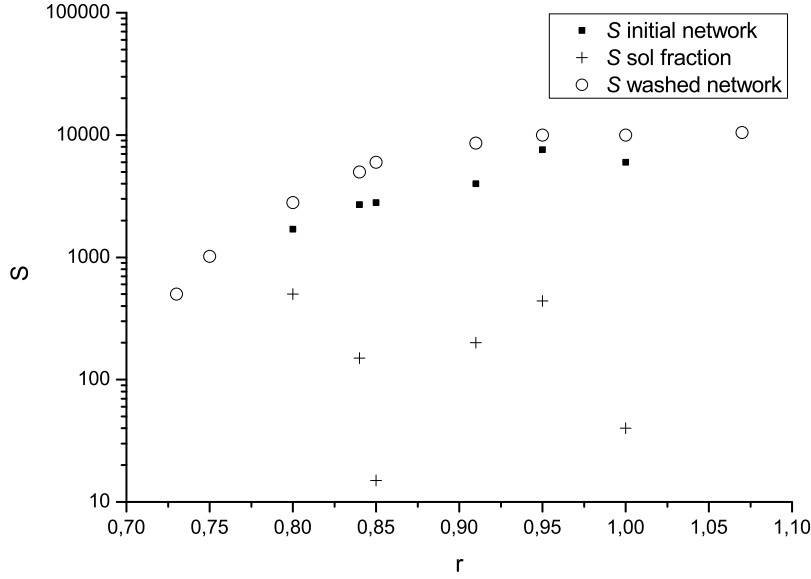
**Fig. 6**  $G_0$  determined from the fits of Equation 4 and 5 to the dynamic moduli as a function of  $r$

to Jensen et al. (2009) we observed  $n > 1/2$  for very soft networks, and when  $r$  is increase to 1 and beyond  $n$  decreases to around 0.30. It is also obvious from the determined values of  $n$  that  $n$  for the initial networks and the washed networks differs the most at low values of  $r$  where the large sol fraction really softens the initial network.

$G_0$  for the networks, see Figure 6, showed that they were very soft compared to traditional silicone networks which are prepared with cross-linkers of higher functionality ( $f > 3$ ) (Mark and Llorente, 1980). The moduli of the investigated initial networks are in the order of  $10^2 - 10^4$  Pa. This is easily explained by the properties of the 3-functional cross-linker which requires that *all* the reaction sites on the cross-linker have reacted and that all the polymers are reacted with the infinite network in both ends in order to be elastically active. If only two chains are connected to the cross-linker, the cross-linker will in fact only act as a chain extender and therefore not act as a cross-linking point. The introduction of chain extenders will hence lead to rapid decrease in the resulting modulus compared to a fully cross-linked network.

### 3.3 Calculating the Weight Fraction of Elastic Chains and Sol and $M_n$ for the Sol Fraction

Villar et al. (1996) published results where the molecular structure of a network (network, pendant chains and sol) was investigated. They developed a model to



**Fig. 7** The gel stiffness,  $S$ , determined from the fits of Equation 4 and 5 to the dynamic moduli as a function of  $r$

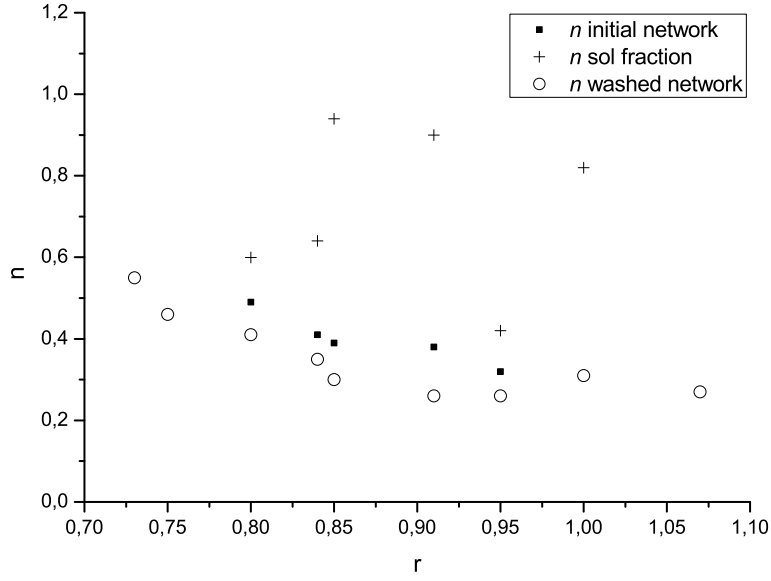
determine the amount of sol. This technique has been applied to the work presented here to check if the investigated system followed the theory. Villar et al. (1996) considered a system of mono- and bifunctional polymers with elastic chains, pendant chains and soluble material (sol). The set of equations used here are simpler since there is only bifunctional polymers (PDMS with two vinyl endgroups) and only the network (elastic and pendant chains) and the sol will be considered as there is no way to separate dangling ends and network into two fractions. Thus our network is formed by mixing PDMS with functional end groups ( $B$ ) and a tri-functional cross-linker ( $A_3$ ). Using the terminology of Villar we obtain that the probability that looking out from an  $A$  group the reaction leads to a finite or dangling chain rather than to the infinite network,  $P(F_A^{out})$ , is given by:

$$P(F_A^{out}) = \frac{1 - rp^2}{rp^2} \quad (8)$$

where  $p$  is the extent of reaction with respect to either A or B groups and  $p = p_A = \frac{p_B}{r}$ . For the PDMS-system it is assumed that the reaction goes to completion and hence  $p_A = 1$  as long as  $r \leq 1$ . For  $r > 1$  then  $p_B = 1$ .

The probability that looking out from a  $B$  group the reaction leads to a finite or dangling chain rather than to the infinite network,  $P(F_B^{out})$ , is given by:

$$P(F_B^{out}) = 1 + rp(P(F_A^{out})^2 - 1) \quad (9)$$



**Fig. 8** The relaxation exponent,  $n$ , obtained from fitting Equations 4 and 5 to  $G'$  and  $G''$

We define the network fraction, ( $W_{net}$ ), as:

$$W_{net} = W_e + W_p \quad (10)$$

where  $W_e$  is the elastically active weight fraction and  $W_p$  is the pendant chain fraction.

The elastically active fraction can be calculated from:

$$W_e = W_{A_3} [(1 - P(F_A^{out}))^3 + 2P(F_A^{out}) \cdot (1 - P(F_A^{out}))^2] + W_{B_2} (1 - P(F_B^{out}))^2 \quad (11)$$

where  $W_{A_3}$  is initial weight fraction of  $A_3$  and  $W_{B_2}$  is the initial weight fraction of  $B$ .  $W_{A_3}$  is given by:

$$W_{A_3} = \frac{M_{nA_3}}{M_{nA_3} + \frac{3}{2r} M_{nB_2}} \quad (12)$$

And  $W_{B_2}$  is given by:

$$W_{B_2} = \frac{M_{nB_2}}{M_{nB_2} + \frac{2r}{3} M_{nA_3}} \quad (13)$$

The pendant chain fraction can be calculated from:

$$W_p = W_{A_3} 3P(F_A^{out})^2(1 - P(F_A^{out})) + W_{B_2} 2P(F_B^{out})(1 - P(F_B^{out})) \quad (14)$$

And finally, the sol fraction can be calculated from:

$$W_{\text{sol calculated}} = W_{A_3} P(F_A^{out})^3 + W_{B_2} P(F_B^{out})^2 \quad (15)$$

In Table 6 the calculated weight fractions of sol can be found along with those found experimentally. The values for  $W_{\text{sol experimental}}$  decrease but seem to find a steady level of 5-10 % when  $r$  approaches 1. The values for  $W_{\text{sol calculated}}$  decrease steadily to 0 (when  $r = 1$ ) and thus do not describe the experimental observations. The reason for this can be that either the theory does not fully describe what is observed or that there are some problems with the used polymers - such as inactive chains, chains with only one active site etc. as mentioned earlier.

**Table 6** The calculated and experimentally determined sol fractions. The sol fraction is calculated by use of Equation 15. In the performed calculations  $M_{nA_3} = 28000$  g/mol and  $M_{nB_2} = 330$  g/mol

$r$	$W_{\text{sol calculated}}$	$W_{\text{sol experimental}}$
0.73	0.1363	0.489
0.75	0.1107	0.068
0.80	0.0622	0.077
0.84	0.0361	0.086
0.85	0.0310	0.108
0.91	0.0097	0.171
0.95	0.0028	0.088
1.00	0	0.103
1.07	0	0.064

## 4 Conclusion

We observed that it was possible to extract an elastic network from a sample which initially showed viscous properties. The sol fraction of the specific sample was able to totally smear out the elastic response from the formed network. We also were able to isolate samples close to the gel point. These observations were verified by fitting the data to the modified gel equation. In general the gel equation could be fitted to the data and the obtained variables  $S$ ,  $n$  and  $G_0$  depend on  $r$  in the expected ways, so  $G_0$  and  $S$  increase with increasing  $r$  while  $n$  decreases.  $G_0$  is related to the elasticity and  $S$  to the trapped entanglements in the network and both of these will increase with  $r$  since more and more chains are attached to the network and the complexity of the network structure is more developed.  $n$  is related to the dynamics of the network and therefore decreases when  $r$  increases because the mobility of the chains is hindered. All in all we observed that  $n > 1/2$  for very soft networks and for harder networks  $n$  decreases to around 0.30, which correlates with values from the literature (Jensen et al, 2009).



We calculated the amount of sol and compare this with experimental results. However we observed that the theory could not describe what we observed in the lab and in general  $W_{\text{sol experimental}}$  is larger than  $W_{\text{sol calculated}}$ . We expect that the primary reason for this is impurities in the PDMS-polymer (such as inactive species, chains with only one active site etc.). The amount of impurities should be 1 % but we estimate that it is significantly higher.

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